

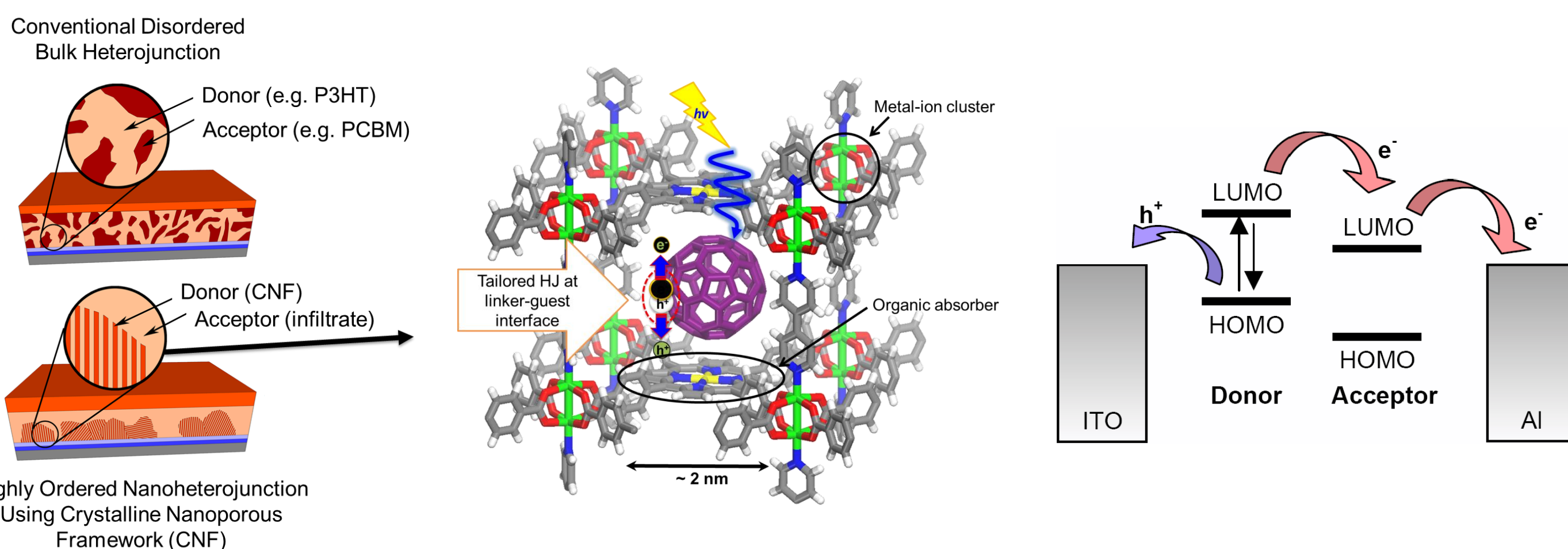
First-Principles Investigation of Metal-Organic Frameworks for Photovoltaics

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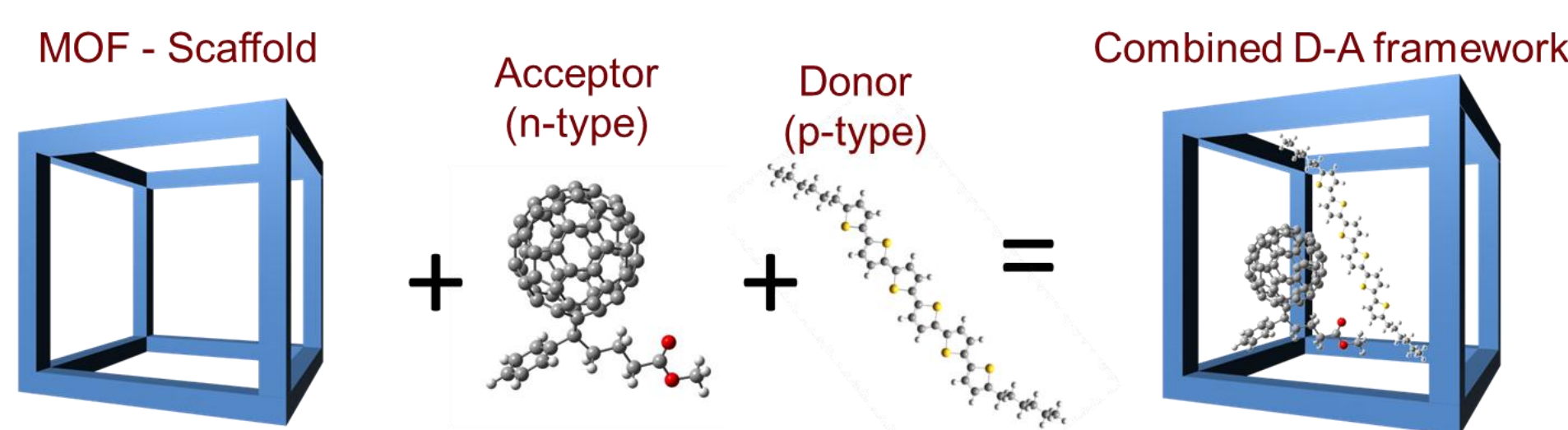
Introduction

Organic and hybrid-organic materials continue to show great promise as next-generation photovoltaics, but the poorly ordered donor-acceptor heterojunction interfaces in these materials are still a major source of inefficiency. The use of metal organic frameworks (MOFs) is a natural step towards controlling nanoscale donor/acceptor interfaces due to the inherent ordering and self-assembly of these porous crystalline frameworks. First-principles calculations (DFT and TD-DFT) have been used to study the energetics of infiltration, preferred orientation, and energy/charge transfer mechanisms of various donor/acceptor molecules within the framework. In addition, DFT has been used as a screening tool to identify potential semiconducting MOFs.

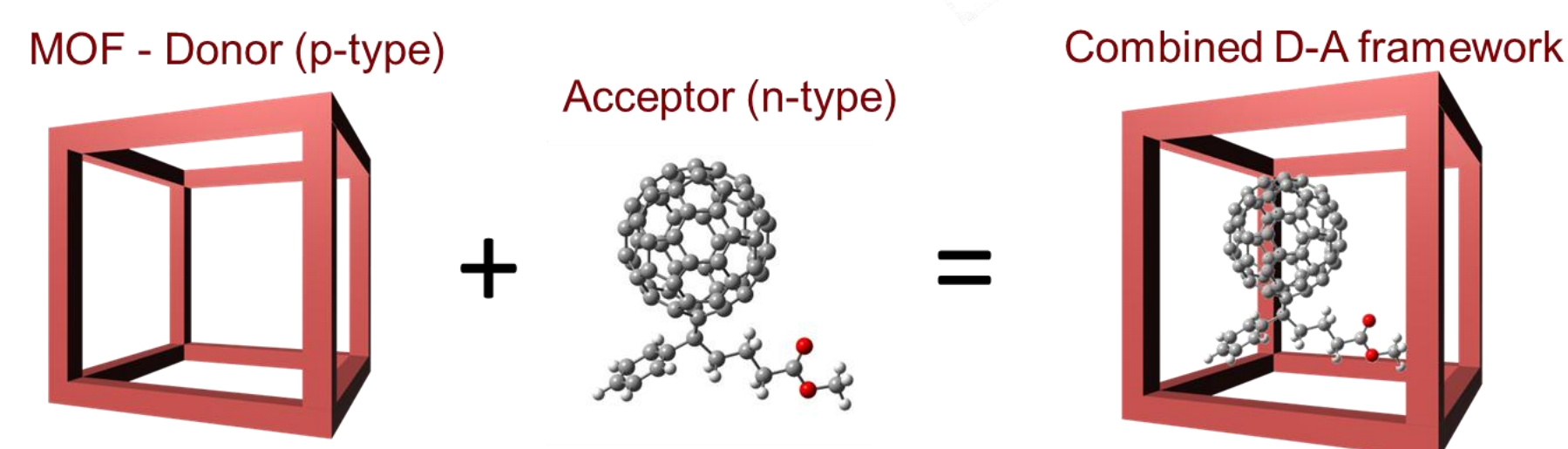


Active Frameworks and Passive Scaffolds For Nano-HJ Active Layers

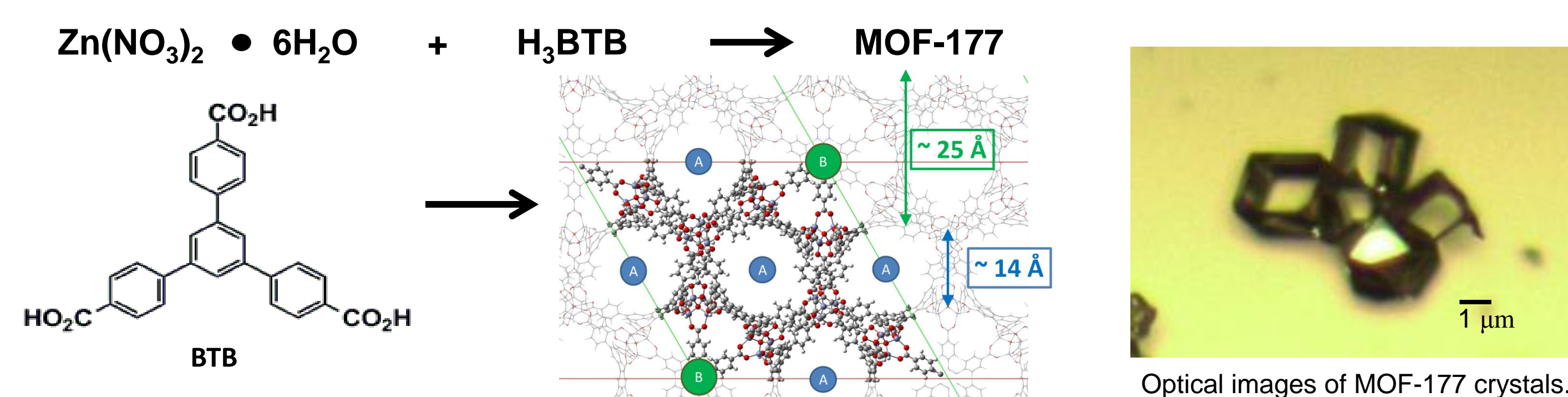
Passive Scaffolds - the MOF simply functions to order the donor/acceptor materials and plays no active role in the PV energy conversion process.



Active Network - the MOF is designed to play an active role in the PV energy conversion process by functioning as the donor or acceptor material.

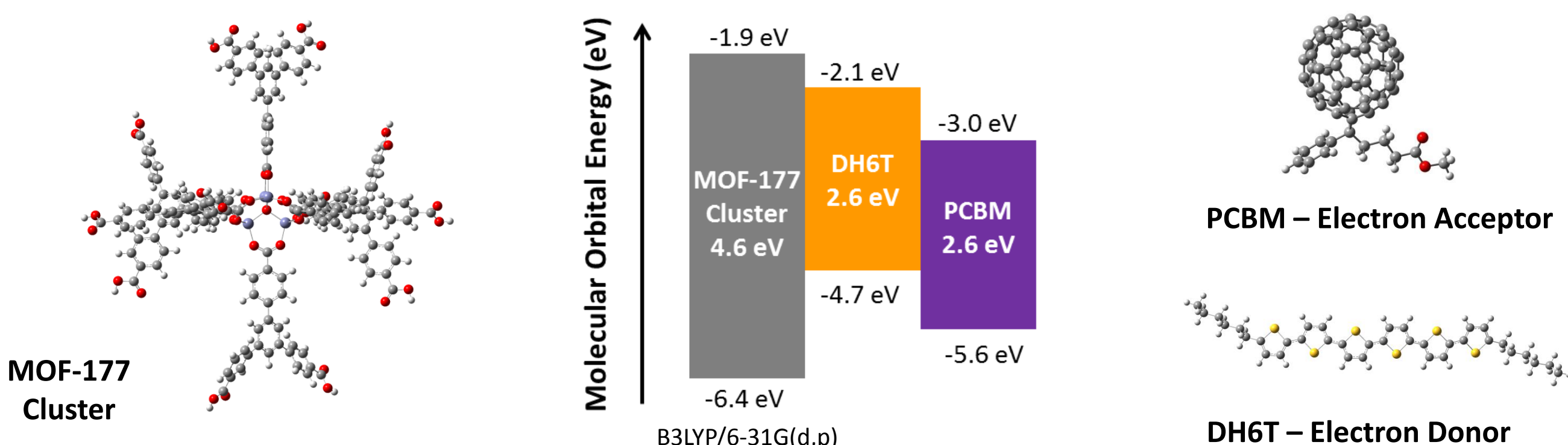


MOF-177 - Structure



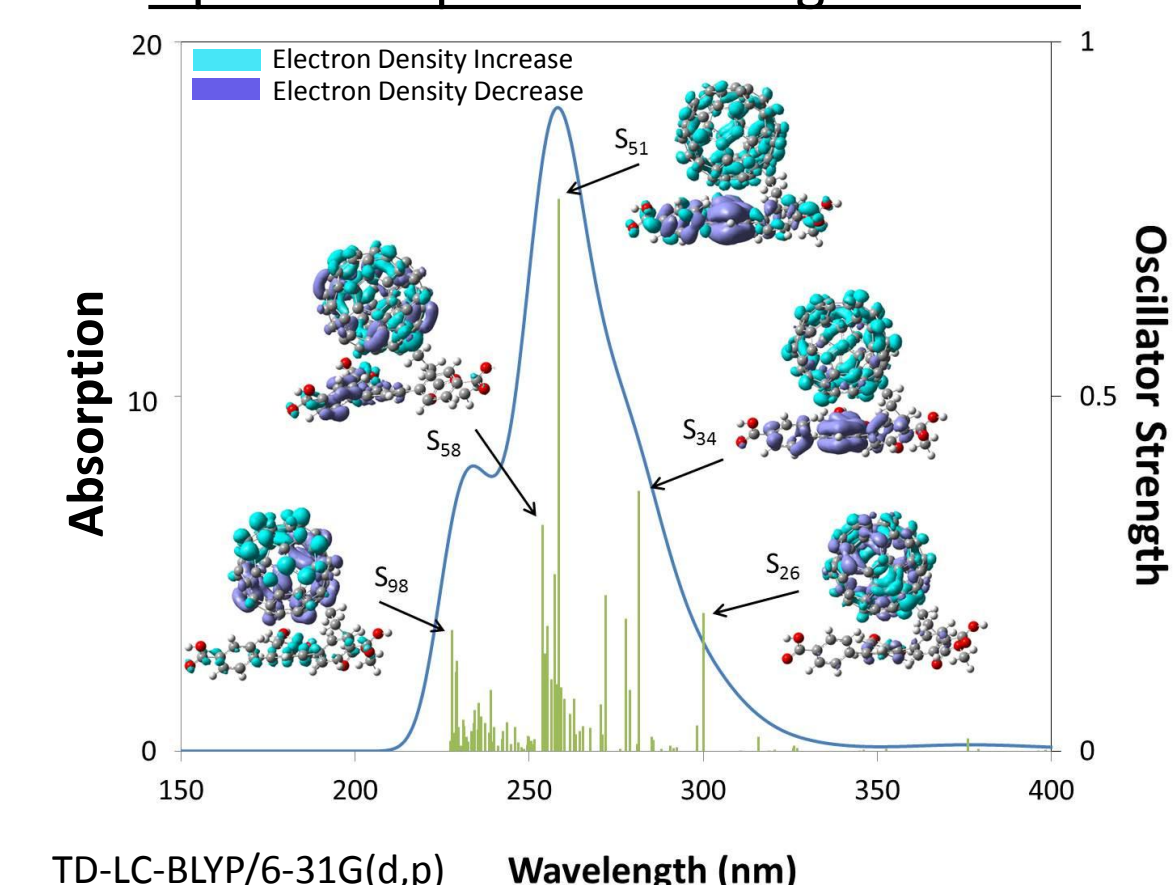
DFT & TDDFT- Electronic & Optical Properties

Electronic Properties (HOMO/LUMO)

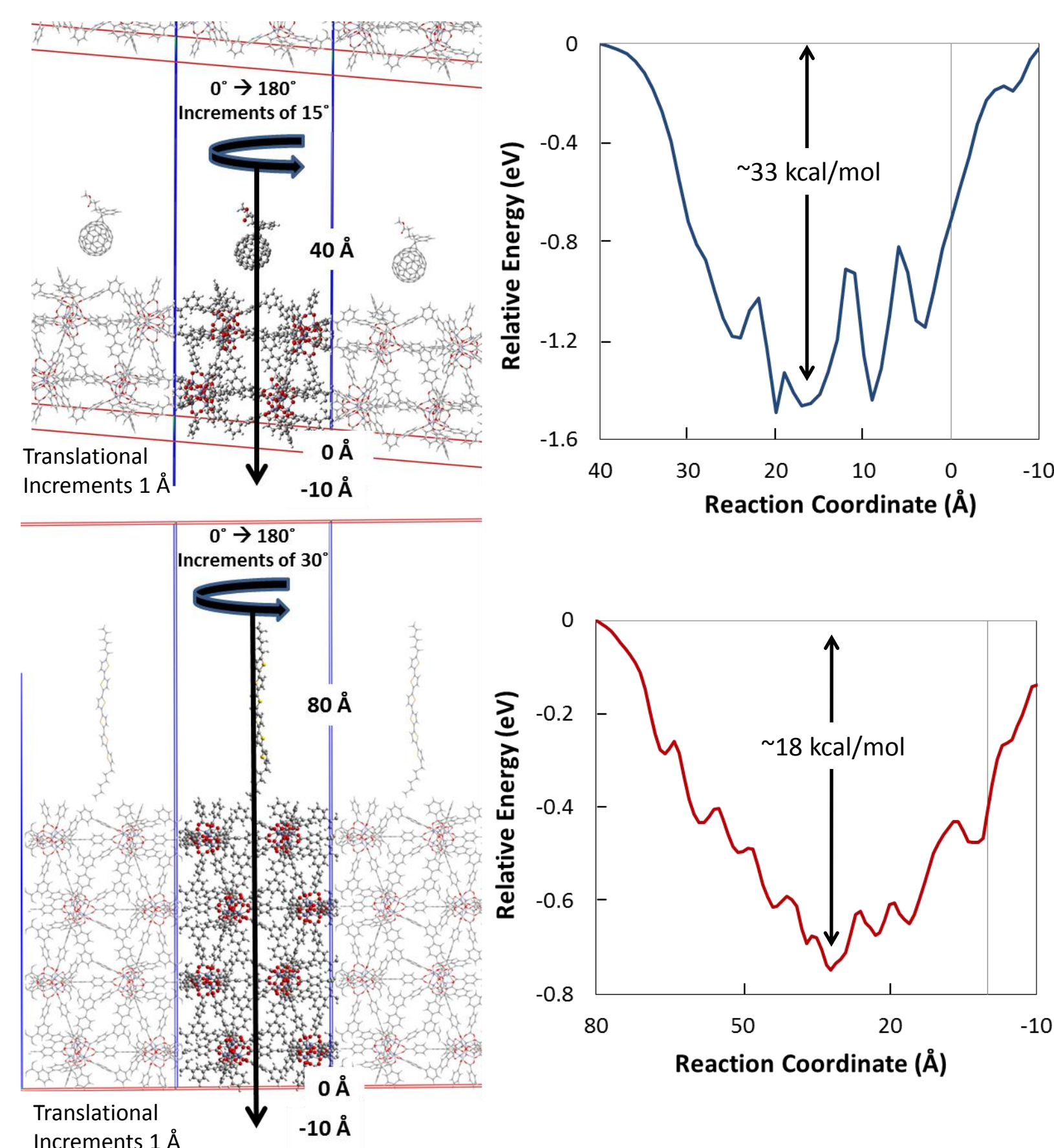


- MOF-177 has a relatively large band gap (~4.6 eV); therefore, is an ideal passive network allowing the infiltrated molecules to control the band gap of the material
- DH6T and PCBM are known donor/acceptor materials with ideal electronic properties; therefore, are ideal candidates for MOF infiltration
- The electron density difference maps (on the left) show that charge transfer can occur between PCBM and BTB (organic linker constructing the MOF); therefore, the MOF could contribute to the electron mobility

Optical Properties - Charge Transfer



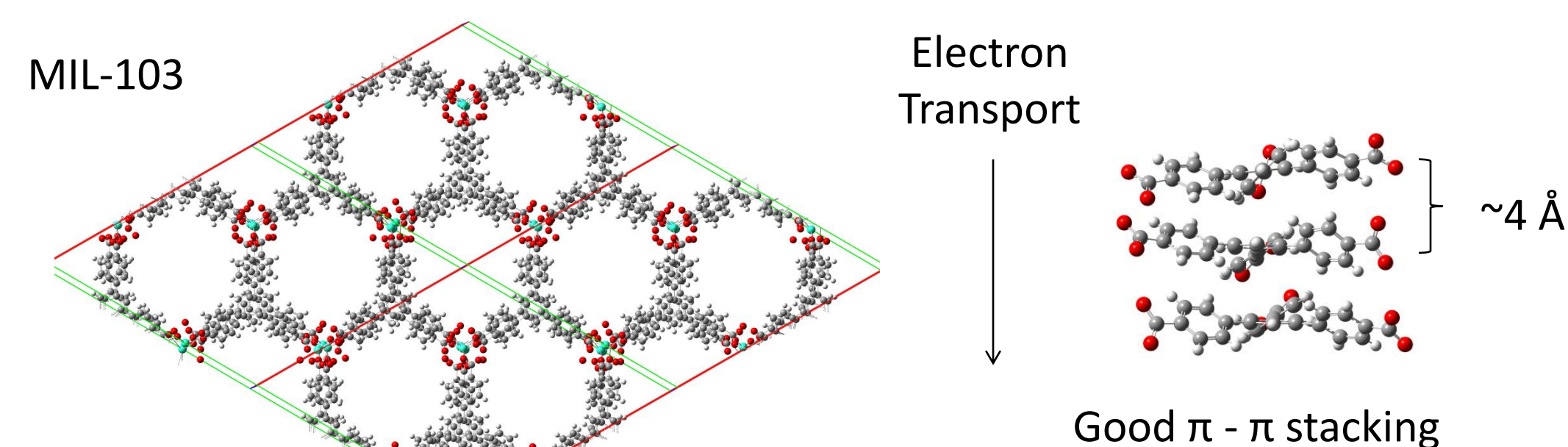
Modeling the Energetics of Infiltration



- Molecular slabs were constructed consisting of 820 and 1628 atoms respectively
- 600+ structures were generated for each system to model the infiltration pathway
- Self-consistent charge density-functional tight-binding (SCC-DFTB) theory was employed
- The potential energy curves indicate that infiltration of MOF-177 with PCBM and DH6T is energetically favored
- Full geometry optimizations were carried out on the lowest energy structures to determine preferred orientation and binding affinities (57 kcal/mol and 40 kcal/mol respectively)

Designing Active (Semiconducting) MOFs

- The linkers must be in close proximity to have efficient electron/hole mobility



However, MIL-103 contains the BTB Linker (i.e. MOF-177) which is not semiconducting

Predicting Electron/Hole Mobility - Marcus-Hush Theory

$$\mu = \frac{eD}{k_B T}$$

$$D = \frac{1}{2n} \sum_{i \neq j} r_{ij}^2 W_{ij} P_{ij}$$

$$W_{ij} = \frac{V_{ij}^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left(\frac{-\lambda}{4k_B T} \right)$$

D - diffusion constant
 e - unit charge
 T - temperature
 k_B - Boltzmann constant

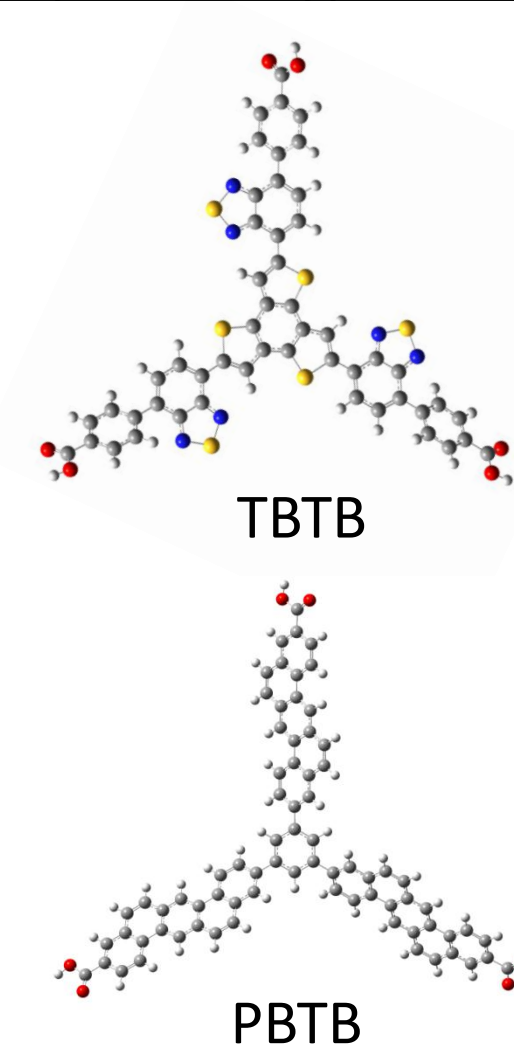
r_{ij} - intermolecular distance
 P_{ij} - hopping probability
 W_{ij} - hopping rate

λ - reorganization energy
 V - matrix coupling element (depends on molecular orbital overlap)

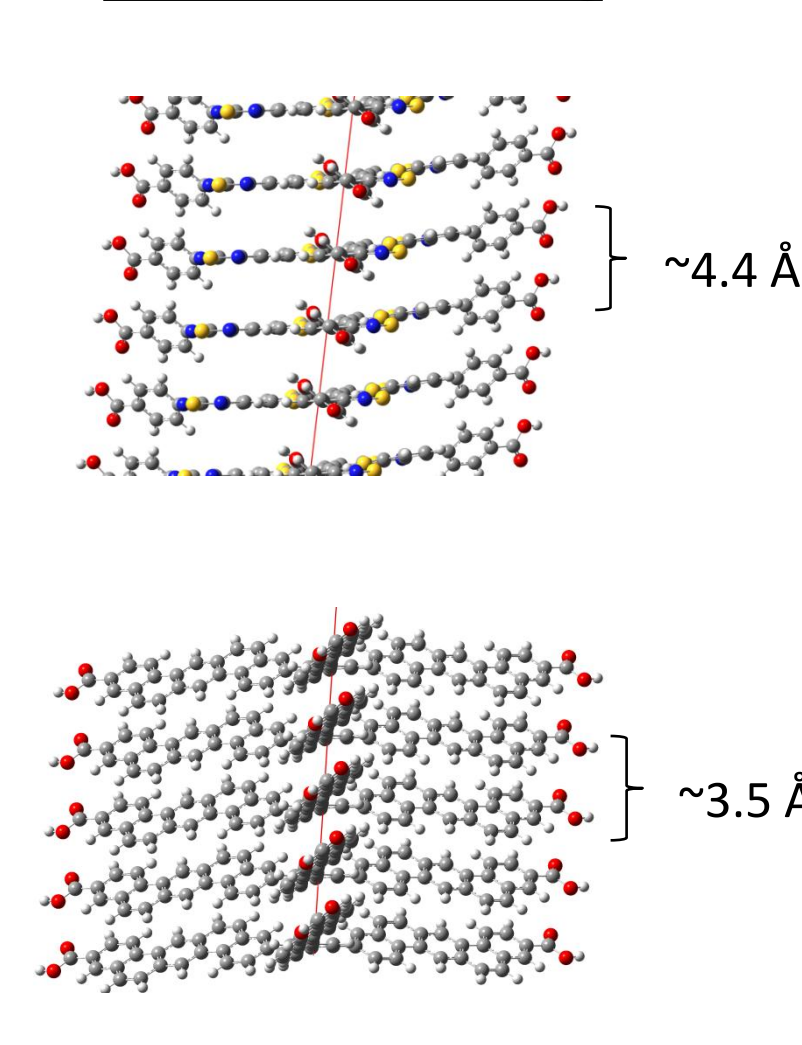
- Charge mobility is directly dependent on intermolecular distance (r_{ij} and V) between the linkers

- The organic linker(s) must have the correct electronic (HOMO, LUMO & band gap) and structural properties

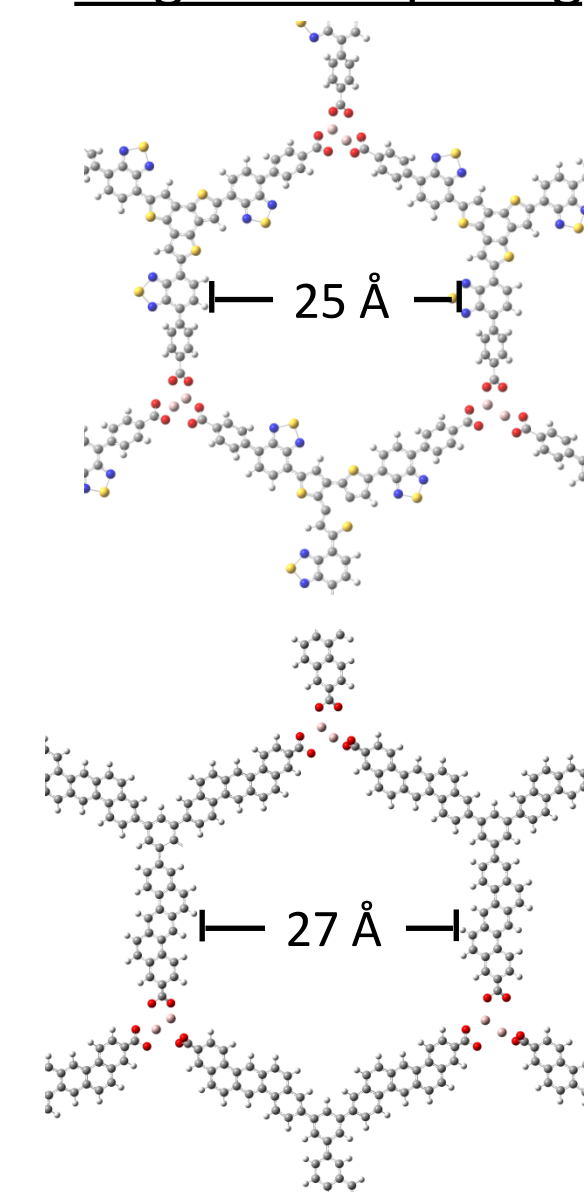
Proposed n-type Linkers



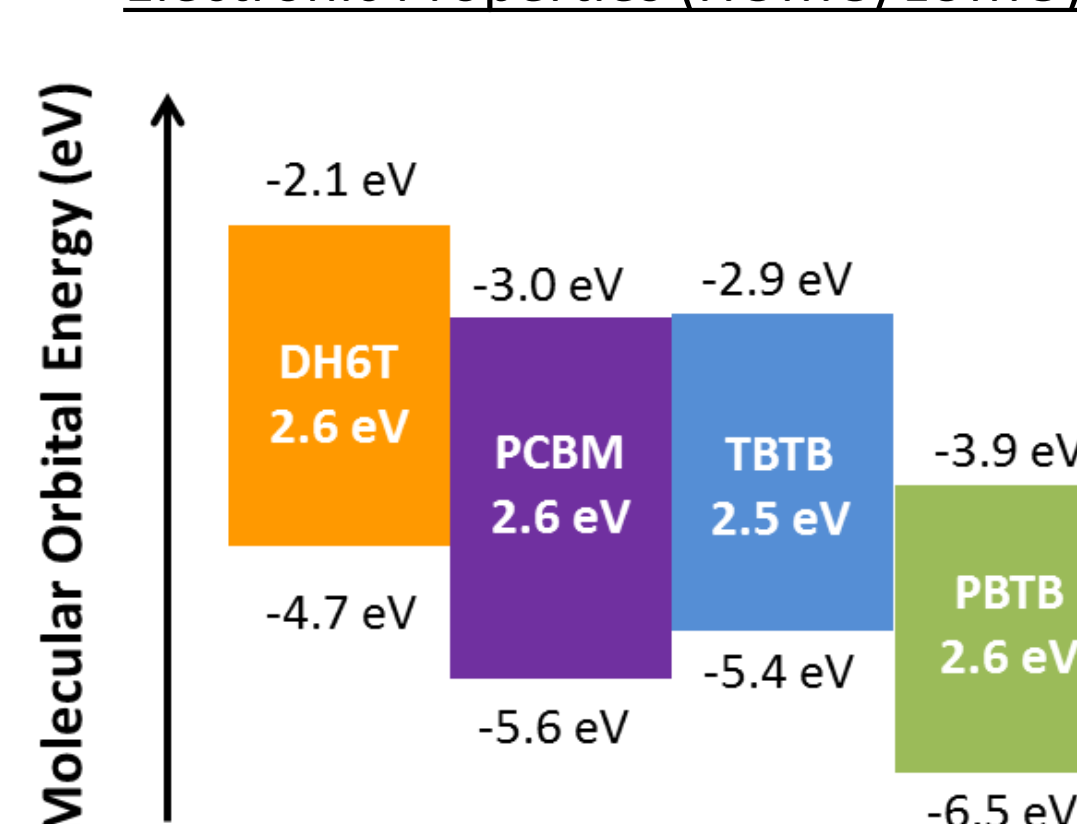
Good π - π stacking



Large Pore Opening



Electronic Properties (HOMO/LUMO)



- MIL-103 has an ideal structural orientation allowing π-π stacking to occur between the organic linkers; however, MIL-103 is not semiconducting because it contains the BTB Linker
- The proposed linkers have the correct structural form (triangular, similar to BTB) allowing the desired MOF architecture to be created
- The relatively large pore sizes will enable infiltration with donor materials (i.e. DH6T)
- The proposed linkers have the essential electronic properties, therefore, are ideal candidates for creating active MOFs